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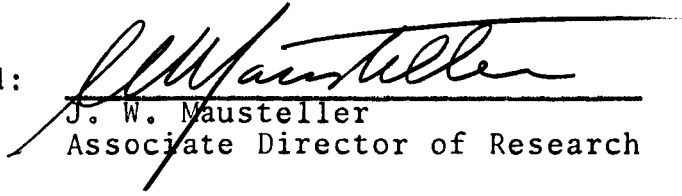
ELECTROLYTIC PRODUCTION OF OXYGEN
AND REDUCTION OF CARBON DIOXIDE

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Sixth Quarterly Status Report
on
ELECTROLYTIC PRODUCTION OF OXYGEN AND REDUCTION OF CARBON DIOXIDE
by
C.A. Palladino and R.E. Shearer

INTRODUCTION

Work during the sixth quarter involved study of the effect of high CO_2 pressures, of new cathode materials, of continuously formed dry amalgams, of reduction promoters and of ion-exchange membranes upon the cathodic reduction of CO_2 in several promising cell combinations. Coulombic efficiencies were also measured for several promising cell combinations in production of formic acid.

EXPERIMENTAL PROCEDURES AND RESULTS

Table 1 is a summary of the conditions and results of the experiments conducted during this report period. A detailed discussion follows below.

High Pressure Cells

Since reduction of CO_2 to formic acid at 50 atmospheres CO_2 has been reported at an efficiency of 90%(1), such a procedure was followed to see if good yields of formic acid might give rise to further reduction to formaldehyde. A pressure cell was constructed from 2 in. diameter stainless steel pipe for runs 185 to 187. A one liter autoclave was adapted for further pressure experiments for runs 192, 192A, 202 and 203.

The steel pipe pressure cell was lined with a polyethylene cup. Mercury, used as the cathode, was placed in the bottom of the plastic liner. This gave an effective cathode area of 8.8 cm^2 . The cathode connection was made by a Teflon insulated platinum-tipped wire through a Conax fitting on the cell cup. The anode was a coiled platinum wire inside a 1/2 in. Teflon tube that was inside a small plastic cup floating on the mercury cathode surface. The electrolyte was at a level two in. from the top of the cell.

(1) Fischer, F. and Prziza, O. Ber. 47 (pt 1) 256 (1914).

TABLE I - SUMMARY OF EXPERIMENTAL RESULTS

Run	Type of Cell	Dimensions	Anode	Anolyte	Diaphragm	Cathode	Catholyte	Time* (hrs)
182	Battery Jar	5" diameter	Pt. wire coil	Li ₂ SO ₄	Porous battery cup	Mercury	Li ₂ SO ₄ CO ₂ flow through dry cathode section	16 23
183	Small H-cell	4" centers	Pt. sheet	5% H ₂ SO ₄ Sat. K ₂ SO ₄	Alundum cup	K amalgam CO ₂ bubbled through wet K-Hg	K ₂ SO ₄	4 1/2 21 28 49 51 63
184	Large H-cell	5" centers	Pt. sheet	5% H ₂ SO ₄ Sat. K ₂ SO ₄	Alundum cup	Mercury CO ₂ bubbled through Hg	K ₂ SO ₄	7 23 1/2
185	Steel pressure 50 atms CO ₂	2" pipe	Pt. wire	Sat. K ₂ SO ₄	None	Mercury	Sat. K ₂ SO ₄	4 7 1/2
186	Steel pressure 50 atms CO ₂	2" pipe	Pt. wire	1% H ₂ SO ₄ K ₂ SO ₄	None	Mercury	1% H ₂ SO ₄ K ₂ SO ₄	3
187	Steel pressure 50 atms CO ₂	2" pipe	Pt. wire	Sat. K ₂ SO ₄	None	Mercury	Sat. K ₂ SO ₄	6
188	2" Glass Pipe	8" centers	Pt. sheet	Sat. K ₂ SO ₄	Ion Exchange Membrane (I)	K-Hg CO ₂ bubbled through K-Hg	Sat. K ₂ SO ₄	4 3/4 19 1/4 27 1/4 49 1/2
189	2" Glass Pipe	8" centers	Pt. sheet	Sat. K ₂ SO ₄	Ion Exchange Membrane (I)	K-Hg CO ₂ bubbled through K-Hg	5% HCOOH K ₂ SO ₄	2 15
190	Small H-cell	4" centers	Pt. sheet	Sat. Li ₂ SO ₄	Alundum cup	Mercury CO ₂ bubbled through Hg	Sat. Li ₂ SO ₄	2 5 29 109
191	Large H-cell	5" centers	Pt. sheet	5% H ₂ SO ₄ Sat. Li ₂ SO ₄	Alundum cup	Mercury CO ₂ bubbled through Hg	Sat. Li ₂ SO ₄	2 11 24 105
192	Autoclave 50 atms CO ₂	1 liter Autoclave	Pt. wire	Sat. K ₂ SO ₄	Alundum cup	Mercury CO ₂ 50 atms	Sat. K ₂ SO ₄	8
192A	Autoclave 50 atms CO ₂	1 liter Autoclave	Pt. wire	Sat. K ₂ SO ₄	Alundum cup	Mercury CO ₂ 50 atms	Sat. K ₂ SO ₄	3 1/2 10 1/2 17 1/2 23 28
193	Autoclave 50 atms CO ₂	1 liter Autoclave	Pt. wire	Sat. K ₂ SO ₄	Alundum cup	Amalgamated Zinc	Sat. K ₂ SO ₄	15

* = cumulative time

I = cation exchange membrane IONAC MC 3142

p = pulsating current; 10 seconds on, 5 seconds off

N = cation exchange membrane Nepton CR-61

Amps.	Volts	Temp.	Tests		Remarks
			Gas Phase Products	Catholyte Organic Product	
0.1p	3.6	Ambient	Cathode CH ₄ neg, CO neg	Neg.	Gas collected in dry section of cathode & flushed into catholyte before samples.
0.1p	3.6	Ambient	Cathode CH ₄ neg, CO neg	Neg.	
0.8	35	Water cooled		HCHO neg, MeOH neg, HCOOH pos.	
0.5	28	Water cooled		HCHO weak pos, MeOH neg, HCOOH pos.	
0.8	35	Water cooled		HCHO weak pos, MeOH neg, HCOOH pos.	
0.8	35	Water cooled		HCHO pos, MeOH neg, HCOOH pos.	
1.5		Cathode 70°C		HCHO weak pos, MeOH neg, HCOOH pos.	
0.5	25	Water cooled		HCHO pos, MeOH neg, HCOOH pos.	
0.8	29	Water cooled		HCHO neg, MeOH neg, HCOOH pos.	
0.5		Water cooled		HCHO neg, MeOH neg, HCOOH pos.	
1.0	18	Water cooled	Cathode CH ₄ neg, CO neg	HCHO weak pos, MeOH neg, HCOOH weak pos.	
1.0	18	Water cooled	Cathode CH ₄ neg, CO neg	HCHO weak pos, MeOH neg, HCOOH weak pos.	
0.5	18	Water cooled	Cathode CH ₄ neg, CO neg	HCHO neg, MeOH neg, HCOOH pos.	Electrode blewout.
0.4	21.5	Ice bath	Cathode CH ₄ neg, CO neg	HCHO weak pos, MeOH neg, HCOOH weak pos.	
0.5	13	Water cooled		HCHO neg, MeOH neg, HCOOH pos.	After 49 1/2 hrs anolyte showed weak positive test for HCOOH.
1.7	13			HCHO neg, MeOH neg, HCOOH pos.	
1.7	13			HCHO neg, MeOH neg, HCOOH pos.	
1.7	13			HCHO neg, MeOH neg, HCOOH pos.	
1.7	19			HCHO neg	Electrolyte pushed into cathode section overnight.
4.5	19				
0.2	19	Water cooled		Neg.	10 cc 10% H ₂ SO ₄ added to catholyte after 5 hrs.
0.15	19			HCHO neg, MeOH neg, HCOOH weak pos.	
0.2	19			HCHO neg, HCOOH pos.	
0.2	19			HCHO neg, MeOH neg, HCOOH pos.	
2	24	Water cooled		Neg.	
1	24				
1	24			HCHO neg, MeOH neg, HCOOH pos.	
1	24			HCHO neg, MeOH neg, HCOOH pos.	
1	5.2	Water cooled	CH ₄ & CO neg.	HCHO neg, MeOH neg, HCOOH weak pos.	Cathode contact wire pushed out of Hg by pressure.
1.2	4.5	Water cooled	CH ₄ & CO neg.	HCHO neg, MeOH neg, HCOOH weak pos.	
2.5	5.5		CH ₄ & CO neg.	HCHO neg, MeOH neg, HCOOH weak pos.	
2.5	5.5		0.04% CO		
2.2	5.7		0.04% CO		
2.2	6.0		0.04% CO	HCHO neg, MeOH neg, HCOOH pos.	
0.1-1.0		Water cooled		HCHO neg, MeOH neg, HCOOH pos.	Cathode broke off. 0.1 amp on overnight to counter galvanic effect. Next morning cell was warm and 1 amp current.

Run	Type of Cell	Dimensions	Anode	Anolyte	Diaphragm	Cathode	Catholyte	Time* (hrs)
194	Nickel beaker	2 1/2" dia.	Ni cup	Sat. Na ₂ SO ₄	Alundum cup	Carbon rod	Sat. Na ₂ SO ₄	4 1/2
195	Beaker	2 1/2" dia.	Pt.unimesh	Sat. Na ₂ SO ₄	Alundum cup	Carbon rod	Sat. Na ₂ SO ₄	4
196	Beaker	2 1/2" diam.	Pt.unimesh	Sat. K ₂ SO ₄	Alundum cup	1" diameter carbon im- pregnated with Hg	Sat. Na ₂ SO ₄	7 11 1/2
197	2" Glass Pipe	8" centers	Pt. foil	Sat. K ₂ SO ₄	Ion Exchange Membrane (N) Heavy	Hg	Sat. K ₂ SO ₄	3 16 28
198	Battery jar	5" diameter	Pt. foil	Sat. K ₂ SO ₄	Alundum cup	Cd Fe mix 3 x 6" plate	Sat. K ₂ SO ₄	5 26 1/2 46 1/2
199	Large H-cell	5" centers	Pt.unimesh	Sat. K ₂ SO ₄	Alundum cup	Cd powder on Ag grid	Sat. K ₂ SO ₄	7 1/2
200	Battery jar	5" diameter	Pt. foil	Sat. K ₂ SO ₄	Alundum cup	Cd Fe mix 3 x 6" plate amalgamated	Sat. K ₂ SO ₄	32
201	Large H-cell	5" centers	Pt.unimesh	Sat. K ₂ SO ₄	Alundum cup	Cd powder on Ag grid amalgamation	Sat. K ₂ SO ₄	32
202	Autoclave 50 atms CO ₂	1 liter autoclave	Pt. wire	Sat. K ₂ SO ₄	Alundum cup	Amalgamated Zn	Sat. K ₂ SO ₄	2 1/2 17 1/2 24
203	Autoclave 50 atms CO ₂	1 liter autoclave	Pt. wire	Sat. K ₂ SO ₄	Alundum cup	Amalgamated Cu	Sat. K ₂ SO ₄	3 6 14
204	Beaker	3 1/2" dia.	Pt.unimesh	Sat. K ₂ SO ₄	Alundum cup	Hg	Sat. K ₂ SO ₄	92
205	2" glass pipe	8" centers	Pt.unimesh	Sat. K ₂ SO ₄	Alundum cup	Hg	Sat. K ₂ SO ₄ 20 gm Ce(SO ₄) ₂ · 10 H ₂ O per liter	100
206	2" glass pipe	8" centers	Pt. foil	Sat. K ₂ SO ₄	Alundum cup	Hg	Sat. K ₂ SO ₄ 10 gm Cobaltic acetate per liter	100

Amps.	Volts	Temp.	Tests		Remarks
			Gas Phase Products	Catholyte Organic Product	
10	6.5	Oil cooled	0.04% CO	HCHO neg, MeOH neg, HCOOH neg.	Cathode gas collected in gas buret. Cathode gas collected in gas buret.
5-10	6-7	Oil cooled	0.07% CO	HCHO neg, MeOH neg, HCOOH neg.	
1	3.4	Ambient	Cathode CH ₄ & CO neg.	HCHO neg, MeOH neg, HCOOH neg.	
1	3.5	Ambient	Cathode CH ₄ & CO neg.	HCHO neg, MeOH neg, HCOOH neg.	
1.0	15	Oil cooled		Neg.	Osmosed into catholyte (about 1/2 of anolyte)
.35	6			Neg.	
.35	6			Neg.	
1.4	6.2	Water cooled		Neg.	
1.4	6.2			Neg.	
1.4	6.2			Neg.	
0.8	13	Oil cooled		Neg.	
1.5	6.2	Water cooled		Neg.	
0.5	7.0	Oil cooled		Neg.	
1.5	4.6	Water cooled		Neg.	
0.1	3.1		0.07% CO		
1	4.1		0.02% CO	Neg.	
1	4.1	Water cooled	0.04% CO		HCOOH sl. pos. anolyte and catholyte
1	4.1		0.03% CO		
1	4.1		Trace CO		
25	5.3	Water cooled		HCHO neg, HCOOH pos.	
1	14.8	Water cooled		HCHO neg, HCOOH weak pos.	
1	12.0	Water cooled		HCHO neg, HCOOH weak pos.	

The Teflon tube that contained the anode wire was attached to a Conax fitting that extended through the cell cap and into a sight glass. As electrolysis proceeded the anode gas displaced the electrolyte in the sight glass and served as an indication of liquid levels. The cathode gas would collect above the electrolyte in the cell. This arrangement allowed for separation of the gaseous products, pressure, and liquid level control. Three runs were made in this cell but work was terminated with the steel pipe cell when the autoclave was ready for the high pressure work. A saturated K_2SO_4 solution at a mercury cathode and a current of 1 amp for 11-1/2 hours and 0.4 amps for 6 hours gave a positive test for formic acid in runs 185 and 187. An acid electrolyte, saturated K_2SO_4 in 1% H_2SO_4 was used in run 186 and after 3 hours at 0.5 amp a positive test for formic acid was obtained. Quantitative results were not obtained on the steel pipe pressure runs but some results were obtained from autoclave runs as noted below.

A one liter autoclave was adapted for use as a pressure electrolysis cell. The autoclave was equipped with a stirrer that provided agitation of the K_2SO_4 electrolyte during electrolysis. Anode and cathode connections were made through insulated packings. The gas phases were not separated in this cell but provisions were made for sampling. The autoclave was operated at 50 atmospheres CO_2 pressure in runs 192-193 and 202-203. Mercury in an alundum cup (cathode area 13.8 cm^2) was used as the cathode for runs 192 and 192A.

An amalgamated zinc cathode was tested in runs 193 and 202 and an amalgamated copper cathode was used in run 203. The copper and zinc cathodes were formed into a hollow cylinder from sheet metal and were set inside an alundum cup. The cylindrical cathodes were amalgamated with a 5% solution of $HgCl_2$, and had areas of 232 cm^2 .

Positive tests for formic acid and negative tests for formaldehyde were obtained in all but run 202 with the zinc cathode. Carbon monoxide was found in the gas phase of all the autoclave runs except 192. Quantitative results expressed as coulombic efficiency showed an efficiency of 11.7% for run 203 with the amalgamated copper cathode, 0% with the amalgamated zinc cathode and 0.16% at the mercury cathode. A comparison with efficiencies of other cells is shown in Table II.

TABLE II - QUANTITATIVE RESULTS

Run No.	CO ₂ Pressure Atmos.	Cathode	Catholyte	Anolyte	Current Density a/cm ²	HCOOH Content g/cc x 10 ³	Coulombic Efficiency (%)
183	1	Hg-K	K ₂ SO ₄	5% H ₂ SO ₄ in sat. K ₂ SO ₄	0.25-0.16	7.36	0.8
184	1	Hg	K ₂ SO ₄	5% H ₂ SO ₄ in sat. K ₂ SO ₄	0.03-0.05	11.08	19.8
190	1	Hg	Li ₂ SO ₄	Li ₂ SO ₄	0.06	5.55	1.6
191	1	Hg	Li ₂ SO ₄	5% H ₂ SO ₄ in sat. Li ₂ SO ₄	0.06	2.02	1.0
192	50	Hg	K ₂ SO ₄	K ₂ SO ₄	0.07	1.32	0.16
202	50	Hg-Zn	K ₂ SO ₄	K ₂ SO ₄	0.0004 to 0.006	0	0
203	50	Hg-Cu	K ₂ SO ₄	K ₂ SO ₄	0.0043	7.12	11.7

Cathode Materials

Cadmium and carbon were tested as cathodes in several experiments. Cadmium was tried without success in earlier work in rod form but in runs 198 to 201 the cadmium used was in a different physical form. Saturated K_2SO_4 was used as the electrolyte. For run 198 the cadmium cathode was a plate made by pressing a cadmium iron mix into strips of perforated steel. Cadmium powder pressed into a silver grid was used as the cathode for run 199. These cadmium plates were samples provided by the Electric Storage Battery Company. After testing the plates as received they were amalgamated and used in runs 200 and 201. Results were negative for the cadmium cathode experiments.

Carbon was tried as the cathode in runs 194 to 196. Carbon monoxide (0.04-0.07%) was produced in runs 194 and 196 with Na_2SO_4 as the electrolyte. The cell for 194 was a nickel beaker that also acted as the anode.

A one in. diameter carbon rod was impregnated with mercury and used as the cathode in Na_2SO_4 for run 196. Mercury was forced into the rod by evacuating the rod in a pressure vessel and pressurizing with 800 psig CO_2 . It was thought a high surface area of mercury could be attained by this technique. No reduction products were formed other than the small amount of CO in the carbon cathode tests.

Dry Amalgam Cell

Early work indicated formic acid formed readily with Li salts as electrolytes and since dry amalgam runs had been made using Na and K salts, Li_2SO_4 was tested in a dry amalgam cell in run 182. The dry amalgam cell with a Li_2SO_4 electrolyte at a mercury cathode was tested for 23 hours at 0.1 amp pulsating current. CO_2 was bubbled through the dry section of the cell which was flushed into the catholyte before sampling. The gases were collected from this flushing and analyzed. However, the results were negative.

Mercury and Amalgams as Cathodes

Early work with K_2SO_4 and Li_2SO_4 at a mercury cathode resulted in the production of some formic acid by the direct reduction of CO_2 . Run 63 gave this result. Several runs were made in order to obtain some quantitative results, determine the operating variables, coulombic efficiencies and determine if an amalgam is necessary at the cathode in order to initiate the

reduction. K_2SO_4 was used as the electrolyte at a K-Hg cathode in run 183 and yielded a coulombic efficiency of 0.8%. The anolyte in an alundum cup was 5% H_2SO_4 in K_2SO_4 . In run 184 mercury was used as the cathode and a coulombic efficiency of 19.8% was obtained. Formic acid was produced in both cells but only the amalgam cell (run 183) gave a trace of formaldehyde.

In this series of tests two cells with Li_2SO_4 as the electrolyte at a mercury cathode were also tested. Both cells (runs 190-191) produced formic acid but no formaldehyde at a current density of 0.06 amps/cm². Run 191 differed in that a 5% H_2SO_4 - Li_2SO_4 solution was used as the anolyte. Coulombic efficiencies were 1.6% for run 191 and 1.0% for run 190.

These test results indicate that an amalgam at the cathode is not necessary to initiate the reduction of CO_2 to formic acid. Table II shows a comparison of the coulombic efficiencies with known cell variables. An unknown variable in these runs was pH of the cell solutions, since neutral solutions become basic at the cathode and acidic at the anode and since variations in remixing are unavoidable. The effect of pH on the CO_2 reduction was not studied and it may be in a very narrow pH range in which reduction of the CO_2 is accomplished.

Ion Exchange Membranes

It was thought formic acid might be oxidized at the anode as fast as it was being formed at the cathode and prevent the further reduction to formaldehyde. A run (188) was made using the glass pipe cell with an ion exchange membrane to separate the anolyte and catholyte. A mercury-potassium amalgam was used in a saturated K_2SO_4 electrolyte. Formic acid was formed at the cathode after 4-3/4 hours at 0.5 amps but was not detected at the anode until 45 additional hours of electrolysis at 1.7 amps. The ion exchange membrane was shown to be effective in delaying the transfer of formic acid to the anode. However, reduction to formaldehyde was not observed at the cathode.

Run 189 continued the series with ion exchange membranes. This cell was set up with a catholyte of 5% $HCOOH$ in saturated H_2SO_4 at a K-Hg cathode. It was thought that since formic acid is readily produced in small quantities by the direct reduction of CO_2 a large excess of formic acid would facilitate the reduction to formaldehyde. The make-up for the formic acid reduced to formaldehyde would be by the direct CO_2 reduction. Thus, a two step reduction would result in the continuous formation of formaldehyde. However, upon electrolysis the anolyte

diffused into the catholyte. A second cell was set up for run 197 and a heavier ion-exchange membrane was used. During the 28 hours electrolysis of a catholyte of 2% HCOOH in saturated K_2SO_4 solution at a Hg cathode, osmosis again took place. The solutions showed no formaldehyde produced.

Reduction Promoters

Since early work with reduction promoters (Runs 54, 65-8, 88) was not done on cells found later to be optimum, runs were made in this period on cells with mercury electrodes and potassium sulfate with reduction promoters added. Cobalt acetate was added to the catholyte in run 206 and ceric sulfate in run 205. No beneficial results were observed.

SUMMARY AND CONCLUSIONS

Coulombic efficiencies in the production of formic acid from carbon dioxide were measured in several promising cell combinations with mercury and amalgam cathodes and sulfates of Li or K as electrolytes and were found to run as high as 20% in one combination and as low as 0.16% for one cell with a mercury cathode and 0% for one with an amalgam.

No improvement in reduction was obtained with use of high CO_2 pressures, of continuously formed dry amalgams, of reduction promoters, of ion exchange membranes, or of cadmium or carbon cathodes.

FUTURE WORK

With the expiration of time allotted to this project expiring April 30, no future experimental work is planned. The data over the whole project will be organized in final form and a final report written.